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Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. 73 (1) 97–111 (2008) UDC 546.284–31:539.23:621.928.46+542.9+543.4
JSCS–3691 *Original scientific paper*

The charge percolation mechanism and simulation of Ziegler–Natta polymerizations. Part VII. Effects of the distribution of chromium active centers on silica on the polymerization of ethylene

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(Received 22 September 2006, revised 13 June 2007)

Abstract: The charge percolation mechanism (CPM) of olefin polymerization in the presence of transition metal compounds has been applied to explain the polymerization of ethylene by silica supported chromium oxide. In the previous work of this series, the fundamental issues and mechanism of this polymerization were presented. In this work the compatibility of the CPM with the empirical findings is confirmed. The CPM has been applied to explain: the appearance of an induction period; the deactivation of active centers and the formation of oligomers; the effects of chromium concentration on the silica surface, the silica surface discontinuity and the pore size of silica on polymerization and the formation of the structure of polyethylene. A mathematical model has been derived to explain the effects of the CrO_x/SiO_2 ratio on the productivity of Phillips catalysts in the polymerization of ethylene. The empirical findings have also been confirmed by computer simulations.

Keywords: ethylene polymerization; Phillips CrO_x/SiO_2; charge percolation mechanism.

INTRODUCTION

Despite the fact that ethylene polymerization by silica supported chromium oxide was discovered some fifty years ago[1] and has attracted a great deal of academic and industrial research, there are still many open questions concerning: (1) the oxidation state of an active center, (2) the mechanisms of initiation, (3) the mechanism of polymerization, (4) the physico–chemical state of Cr species at the silica, (5) the polymerization kinetics, particularly the occasional appearance of an induction period, (6) the origin of the structure and very broad molecular

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doi: 10.2298/JSC0801097S

weight distribution (MWD) of PEHD, (7) the role of silica and the correlation of its properties with the results of polymerization.

Hence, in the previous work of this series,[2] the fundamental issues of ethylene polymerization by silica supported chromium oxide were analyzed and the charge percolation mechanism (CPM), which has recently been applied to explain olefin polymerization by other Ziegler–Natta transition metal complexes, was suggested. It was explained that starting from Cr precursors, after their immobilization on the silica, thermal treatment and the addition of ethylene (or CO), various immobilized Cr(II) and Cr(IV) species are produced, which exist simultaneously at the SiO_2 (Scheme 1). These species, Cr(IV) and Cr(II), are unstable. There is a tendency to equalize their oxidation states to Cr(III) by charge transfer from Cr(II) to Cr(IV), but this cannot occur since they are immobilized and highly separated on the support. The immobilized Cr(II) to Cr(IV) species on the support are gradually surrounded by an adsorbed monomer film (Scheme 1, top). A cluster of monomers, with overlapping π-bonds, connects the two immobilized Cr species. Once a bridge is completed (the percolation moment), a charge transfer occurs. The whole π-electron cloud in the monomer cluster will be pulled toward the Cr(IV), since it has a more positive charge than Cr(II). This displacement of π-electrons attracts a proton from an alkyl group of a Cr(IV) to the terminal monomer molecule, leaving an electron pair on the alkyl group. Simultaneously, a partially positive charge is formed on the terminal monomer molecule coordinated to Cr(II), a proton from the terminal monomer molecule is repelled to Cr(II). The electron pair, left on the terminal monomer molecule, enables the simultaneous polymerization of all the monomer molecules forming the bridge between Cr(II) and Cr(IV). Both Cr species equalize their oxidation states simultaneously with the polymerization of monomer (Scheme 1, bottom). The polymer chain is removed from the support making its surface free for subsequent monomer adsorption. The whole process is repeated by the oxidation–reduction of another Cr(II)–Cr(IV) ensembles immobilized on the support.

$$[\mathbf{Cr(II)}\cdots CH_2{=}CH_2\cdots(CH_2{=}CH_2\cdots)_nCH_2{=}CH_2\cdots\mathbf{Cr(IV)}\cdots(CH_2{=}CH_2)]/\mathbf{SiO_2} \rightarrow$$
$$\rightarrow [H{-}\mathbf{Cr(III)}\cdots\ \cdots\cdots\cdots\cdots\mathbf{Cr(III)}{-}CH{=}CH_2]/\mathbf{SiO_2} +$$
$$+\ CH_2{=}CH{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_3$$

Scheme 1.

In the previous work,[2] using this mechanism, the answers to questions (1) to (4) cited above were given. The aim of this article is to show that the CPM is compatible with the empirical findings and to give the answers to the remaining questions (5) to (7) listed above. The origins of the induction period, as well as the effects of the distribution of Cr on the silica support on the productivities of Cr and silica are presented.

COMPATIBILITY OF THE CPM WITH EMPIRICAL FINDINGS

Induction period

An induction period has been noticed in some cases, *i.e.,* when the ethylene and the activated CrO_x/SiO_2 came into contact, the polymerization did not commence immediately or it started very slowly and increased with time.[3] For example, Cr(VI) oxide/silica is not immediately active after being charged into the reaction medium which had previously been saturated by ethylene.[4,5] An induction time up to 80 min has been reported and then the rate of polymerization gradually increased during the run. It was explained that the induction time was probably due to the slow reduction of Cr(VI) by ethylene to an active lower valence species and the increase in rate due to the slow alkylation step. On the contrary, if $Cr(II)/SiO_2$, obtained by the reduction of Cr(VI) by CO, is brought to contact with ethylene, the polymerization commences almost immediately.[6,7] Also, organochromium(II) catalysts come on stream immediately, because they are already reduced and alkylated.

These empirical findings are quite compatible with the CPM which requires Cr(IV)–Cr(II) ensembles to be present on the silica. The transformation Cr(VI) → → Cr(IV) →Cr(II) by ethylene is a slow process performed initially by the partially breaking of two C=O bonds and one C=C bond, followed by the complete breaking of the two remaining C−O bonds and one C−C bond (Fig. 1 in Ref. 2).

In the case of CO pre-reduced Cr precursors, the coordination of ethylene molecules with the pre-formed Cr(II) ions, their alkylation and oxidation (ethylene + Cr(II) → R−Cr(IV)) are fast processes since only one C=C bond has to be partially broken to a C−C bond (Fig. 2 in Ref. 2). Furthermore, the initial surface concentration of Cr(II) ions is high and the average distance between the residual Cr(II) ions and the just formed R−Cr(IV) ions is low. A small amount of ethylene has to be adsorbed to produce Cr(IV) ions and to build a monomer bridge between the just formed Cr(IV) ions and the surrounding residual Cr(II) ions. Hence, the polymerization commences without an induction period, even if the silica coverage by ethylene is low.

According to the CPM, the sequence of the appearance of the percolation participants on the support has a great effect on the polymerization.[8] In the case of Cr(VI) precursors, almost complete silica coverage by ethylene has to be achieved before the Cr(II)−Cr(IV) ensembles are formed and the polymerization begins. This sequence can be classified as an SMA, *i.e.*, support + monomer monolayer formation + active centers ensemble formation. The sequence in the case of CO reduced precursors can be classified as an SAM, *i.e.*, support + active centers formation + monomer monolayer formation.

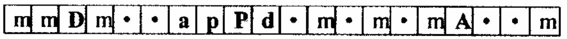
The entropy of adsorbed ethylene decreases with increasing coverage, achieving a minimum value at full coverage.[9] It can be concluded that the higher the entropy of adsorbed ethylene, the shorter is the induction time. Exactly the same effect of ethylene entropy on the induction time has been confirmed in the case of high pressure, free radical polymerization of ethylene.[10] Furthermore, it is a general rule in the theory of organized monomer polymerization, proposed by Kargin and Kabanov,[11] that the induction time increases with increasing monomer organization.

Deactivation of active centers and formation of oligomers

According to the CPM, Cr(II) is an electron donor (**D**) and Cr(IV) is an electron acceptor (**A**). They are immobilized and separated on the support (Fig. 1a). Monomer molecules are gradually adsorbed making a bridge between **A** and **D** (Fig. 1b). No polymer is formed until the bridge between some **A** and **D** is completed. A critical moment appears when the last monomer is adsorbed, thus completing the bridge (at site **P,** Fig. 1c). Such processes are analyzed by the theory of critical phenomena, particularly by the percolation theory.[12]

a) Immobilized acceptors (A) and donors (D) separated by empty sites (•) on the support

b) Monomer (m) adsorption



c) Bridge is completed, polymerized monomer (p), deactivated acceptor (a) and donor (d)

d) Polymer is removed making the free adsorption sites for the additional monomer adsorption between more separated A and D

Fig. 1. Phases of an elementary percolation step of an SAM sequence presented on a segment of a support adsorption row.[8,13] (In this case **A** = Cr(IV), **D** = Cr(II) and **a,d** = Cr(III)).

According to the CPM, the very first bridges have to be formed between an **A** and **D** which are situated close to each other on the support surface (Fig. 1a–c). Subsequently, more separated **A** and **D** sites will be included in the process (Fig. 1d). Consequently, oligomers with a low degree of polymerization (X_n) will be obtained initially, but X_n should increase with increasing polymerization time.[8,13] Simultaneously, the number of active centers (**A** and **D**) remaining on the support should decrease. Experimental data[14] confirmed such predictions of the CPM (Fig. 2, left).

The described processes were computer simulated using the Monte-Carlo method.[13] Two dimensional percolation processes were simulated. (The computer simulation of ZN polymerization by the CPM is explained elsewhere.[8,15]) In the simulation, the Cr(II) and Cr(IV) ions (160000 each) were initially randomly distributed over a part of the support containing 16×10^6 adsorption sites arranged in a hexagonal lattice. Then, ethylene was introduced which gradually and randomly adsorbed on the empty sites. The Cr(II) and Cr(IV) ions were surrounded by growing monomer clusters at the surface. Occasionally, a monomer bridge connects some Cr(II) ion with some Cr(IV) ion. According to the CPM, both ions are transformed to Cr(III) and deactivated. Simultaneously, the monomer molecules of the bridge polymerize and detach from the support. The simulation enables the effects of the quantity of ethylene molecules added to the silica on the change of degree of polymerization and the number of active centers, *i.e.*, Cr(II) and Cr(IV), remaining on the silica to be observed The results of the computer simulation based on the CPM have the same trends as the experimental data (Fig. 2, right). (The numbers of Cr ions and adsorption sites used in the simulations were high enough for reproducible simulations. They were, however, too low in comparison with the real values, since one gram-atom of Cr has 6.023×10^{23} atoms and one gram of silica has several hundreds of square meters, *i.e.*, ≈ 10^{20} adsorption sites for ethylene molecules. Hence, the results of simulation can show only the trends of the various effects but not the real values.)

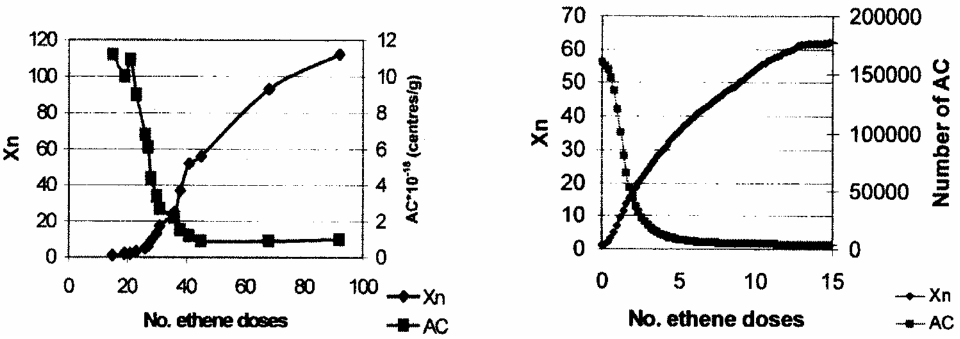


Fig. 2. The mean X_n of ethylene oligomers and the concentration of active centers (AC = Cr(II) + + Cr(IV)) as a function of the quantity of adsorbed ethylene on CrO_x/SiO_2. (Left – experimental data;[14] right – simulation based on the CPM).

Effects of chromium concentration on the silica surface on the polymerization activity

The distance between Cr atoms on the silica is in relation to its surface concentration (Fig. 3). Hogan calculated that the distance between the Cr ions decreased from 16 to 0.65 nm with increasing Cr loading from 0.01 to 6.0 wt. % on a silica having a surface area of 300 $m^2 g^{-1}$ (Table 5 in Ref. 16). The surface concentration (Cr_S) and the average distance between the Cr atoms (L) on a support having a specific surface area (S) can be calculated by the simple Equations (1–3), which give the same values as those presented by Hogan:

$$Cr_S = Cr_0 N/AS \tag{1}$$

$$S_{Cr} = 1/Cr_S \tag{2}$$

$$L = (1/Cr_S)^{0.5} \tag{3}$$

where Cr_s (Cr atoms per m^2 of support) is the number of Cr atom per unit area of support; Cr_0 (g Cr per g catalyst) is the initial mass fraction of Cr in the Cr/SiO$_2$ precursor; N is Avogadro's number; A is the atomic mass of Cr; S (m^2 of support per g catalyst) is the specific surface area of the support; S_Cr (m^2 of support per Cr atom) is the support surface area occupied by one Cr atom; L (m per Cr atom) is the average distance between two Cr atoms on the support.

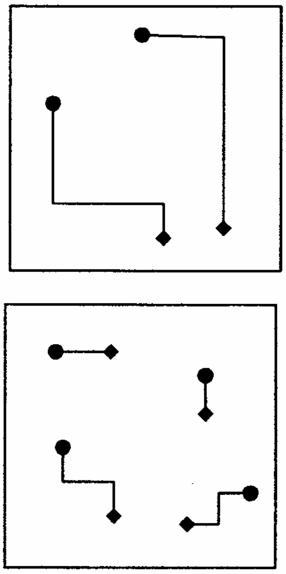


Fig. 3. The percolation path lengths between Cr(II) (•) and Cr(IV) (♦) ions for a low (top) and for a high (bottom) Cr loading.

The productivity of such a catalyst in ethylene polymerization was experimentally determined and presented as chromium productivity (P_Cr) and support productivity (P_S), *i.e.*, the quantity of polyethylene produced per unit of Cr and per unit of support, respectively. It was found experimentally that P_Cr decreased but P_S increased with increasing content of Cr in the SiO$_2$ (Fig. 4, top).[16] Hogan explained that P_Mt decreased since there was a competition for monomer insertion between two Cr ions if the distance between them was very small.

These experiments, however, can be better explained and predicted by the CPM. It is known[14,18,20] that only a small fraction (f) of loaded Cr_0 become an active center, *i.e.*, $f = Cr_\mathrm{activated}/Cr_0 = 0.001 - 0.004$. According to Relations (1–3), the average distance between the active centers (L_a), *i.e.*, Cr(II) and Cr(IV), is given by Relation (4):

$$L_\mathrm{a} = [AS/(fCr_0N)]^{0.5} \qquad (4)$$

The polyethylene yield (g PE per g catalyst) is given by:

$$P = n_\mathrm{p}X_nM_\mathrm{Et}/N \qquad (5)$$

where n_{p} is the number of polyethylene chains per one gram of catalyst; X_n the average degree of polymerization, *i.e.*, the average number of ethylene molecules per one polymer chain; M_{Et} is the molecular mass of ethylene (28 g mol^{-1}).

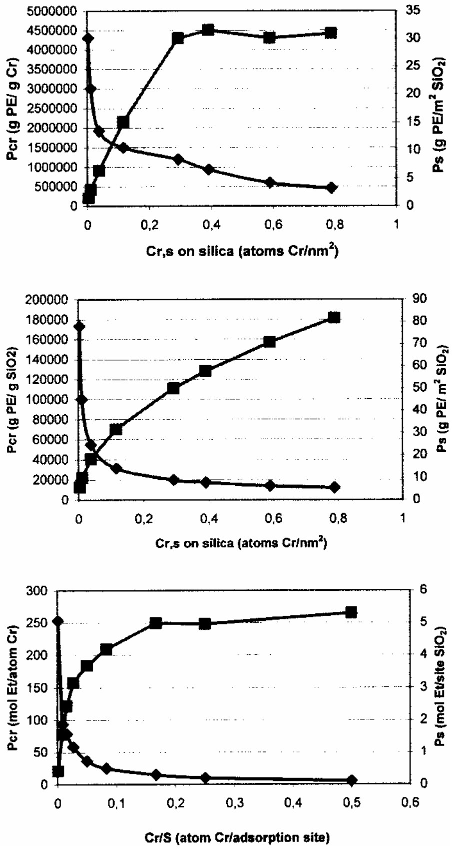


Fig. 4. Chromium (♦) and silica (■) productivities; top – experimental data,[16] middle – calculated by Eqs. (10–11) using K = 10000 (arbitrary value) and bottom – computer simulation (SMA sequence).

According to the CPM, two active centers are deactivated for each polymer chain. Hence the number of polymer chains (n_{p}) is given by Relation (6). X_n is proportional to the distance L_{a} between the active centers, Relation (7):

$$n_{\mathrm{p}} = fCr_0N/2A \qquad (6)$$

$$X_n = kL_{\mathrm{a}} \quad (k \text{ is a coefficient of proportion}) \qquad (7)$$

The productivities of chromium, P_{Cr}, (g PE per g Cr) and silica, P_{S}, (g PE per m^2 SiO$_2$) are:

$$P_{\mathrm{Cr}} = P/Cr_0 \qquad (8)$$

$$P_{\mathrm{S}} = P/S \qquad (9)$$

From Eqs. (4–7), one can derive:

$$P_{\mathrm{Cr}} = (kM_{\mathrm{Et}}/2)\,(f/AN)^{0.5}(S/Cr_0)^{0.5} = K(S/Cr_0)^{0.5} \qquad (10)$$

$$P_S = (kM_{Et}/2)(f/AN)^{0.5}(Cr_0/S)^{0.5} = K(Cr_0/S)^{0.5} \quad (11)$$

where

$$K = (kM_{Et}/2)(f/A\ N)^{0.5} \quad (12)$$

In Eqs. (10–12), only the coefficients k and f are unknown. The plots of the calculated P_{Cr} and P_S (Fig. 4, middle) show the same trends as the experimental ones (Fig. 4, top), using Hogan's[16] experimental values for Cr_0 from 0.01 to 6.0 wt. % and $S = 300\ m^2\ g^{-1}$ SiO_2 and an arbitrary value for K of 10000.

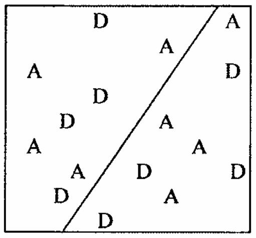
The here derived mathematical formulas are based on the assumptions that all active centers are initially present (SAM sequence) and that the average distances between them do not change during the polymerization. These assumptions are not realistic for the experimental data[16] discussed here. Hence, computer simulations were performed using the SMA sequence of active centers and the monomer appearance on the support. The results of simulations (Fig. 4, bottom) show similar trends as the calculated and as the experimental results.

According to experimental experience, the simplified Formulas ((10) and (11)) and the computer simulation based on the CPM, a high chromium productivity, P_{Cr}, is achieved at low concentrations of chromium and high surface areas of silica.

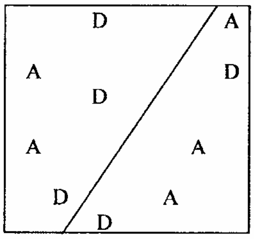
Effects of silica surface discontinuity on polymerization activity

The more separated are the Cr active centers on silica, the higher is P_{Cr}. There is, however, a maximum distance between the Cr(II)–Cr(IV) ensembles which can be bridged by adsorbed monomer. The huge surface area of any silica particle is divided into smaller regions. These regions are separated by pore walls, dislocations and other types of surface imperfections, which make obstacles producing discontinuities in the adsorbed monomer monolayer. The monomer molecules can make a bridge only between those Cr(II) and Cr(IV) ions belonging to the same region. Such phenomena have been explained by the theory of active center ensembles proposed by Kobozev,[19] as a general theory in catalysis. This theory was modified and applied to explain Z–N polymerizations.[15,20] An outline of this concept and its application to explain ethylene polymerization by CrO_x/SiO_2 precursors will be presented here.

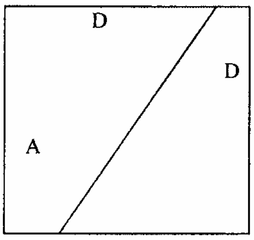
According to the concept of Kobozev, a critical factor is the number of active centers per one region. A schematic presentation of the Cr active centers in two regions, *i.e.*, two pores of silica, is presented in Fig. 5. Each region behaves as an individual "micro-reactor" containing a definite number of active centers. In a case of very high concentrations of active centers (Fig. 5a), according to Eqs. (10) and (11) P_{Cr} should be low while P_S should be high. Decreasing the number of active centers number contributes to an increase of P_{Cr} and a decrease of P_S. According to Kobozev and the CPM,[15] there is an optimal number of active center ensembles (Fig. 5b), contributing to the maximum of P_{Cr}. When the number of Cr active centers is very low (Fig. 5c), some regions become inactive because they contain only one or no active center. Hence, the CPM and the Kobozev theory predict that the values of P_{Cr} and P_S should decrease at the very low concentrations of chromium. This effect has been investigated by computer simulation[8,13,15] (Fig. 6, top) and predicted by a very simple calculation.[13] A sharp maximum of metal productivity ($P_{Mt,max}$) is obtained[15] if the number of active centers is 3 or 5 per surface region in the SAM sequences of one- and two-dimensional percolation processes, respectively, and if the number of Mt(IV) is equal to that of Mt(II). The value of $P_{Mt,max}$ depends on the size of region, *i.e.*, the number of adsorption sites in it – the more sites, the higher is $P_{Mt,max}$.



a) Very high concentration of active centers



b) Optimal concentration of active centers



c) Very low concentration of active centers

Fig. 5. Schematic presentation of two regions, *i.e.*, two pores, with different concentrations of active centers (**D** = Cr(II) and **A** = Cr(IV), the solid lines represent the obstacles between the two regions).

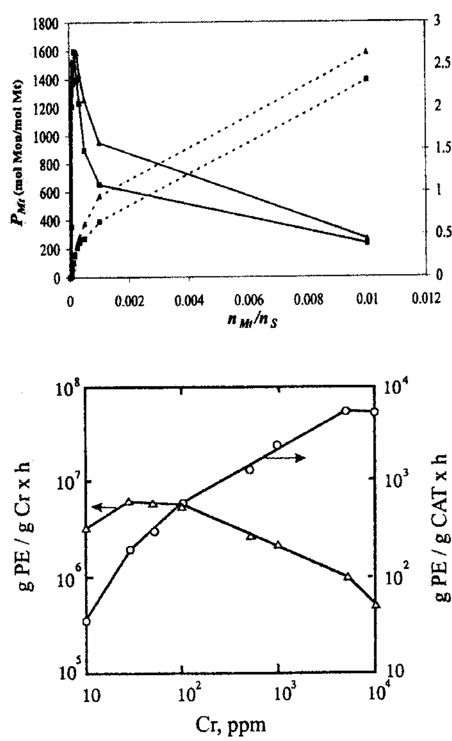
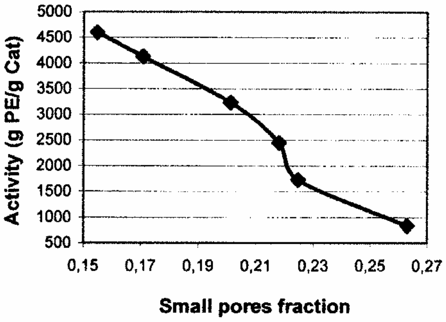


Fig 6. Effects of Mt loading on P_{Mt} and P_S. (Top: prediction by computer simulation; P_{Mt} – solid lines, P_S – dotted lines, ■ – SAM and ▲ – SMA sequences; bottom: experimental data.[1] Note: The trends on the top are similar to the trends on the bottom if logarithmmic scales of the abscissa and ordinate are used instead of linear ones.).

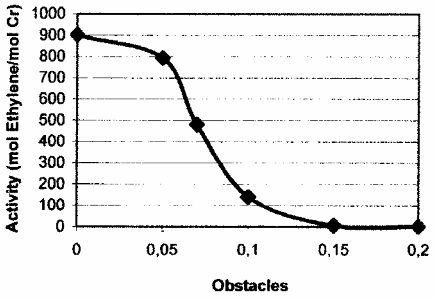
Indeed, detailed experiments[1] on ethylene polymerization by the CrO_x/SiO_2 system showed that the activity per chromium atom reaches a sharp maximum ($P_{Cr,max}$) near a Cr loading of 0.005 wt % (Fig. 6, bottom), although other values have also been reported, *i.e.*, 0.01 wt %. Sharp $P_{Cr,max}$ values were obtained for Cr loadings of 3 and 5 wt % in the case of propylene polymerization.[21] The same effect was noticed in other Z–N polymerization systems.[8,13,15] Several dozens of experiments have been analyzed and explained by the Kobozev theory and by the CPM. Some examples were presented: the ethylene polymerization by CrO_x/SiO_2,[8] propylene polymerization by $TiCl_4/AlEt_3/MgCl_2$, by $TiCl_4/AlEt_2Cl$/graphite and by metallocene/MAO systems.[8,13,15]

Effects of pore size of silica on the polymerization activity

Silicas with small pores are always catalytically inferior and therefore the industrial silicas of choice have an average pore size diameter from 5 to above 20 nm.[22] For example, McDaniel[4] prepared the silicas that had a constant value of surface area (375 $m^2\ g^{-1}$) but with different pore volume size and distribution. It was shown that the activity of the finished catalyst increased with the pore volume. Using the data presented in Table II in Ref. 4, Fig. 7a was prepared to illustrate that the activity decreased with increasing volume fraction of small pores.



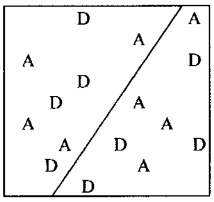
(a) Experimental data



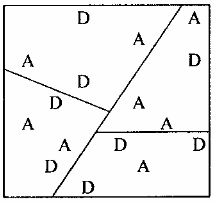
(b) Simulation based on the CPM

Fig. 7. Effect of a small pore fraction of the silica on the polymerization activity: (a) experimental results[4] and (b) computer simulation based on the CPM.

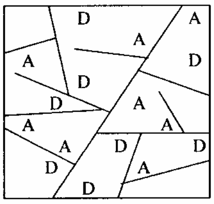
This phenomenon can not be explained by the insertion mechanism, which is generally accepted in Z–N polymerization. It is easy to explain it, however, by the CPM and the Kobozev theory. In the case of large pores, each of them contains a large number of active centers (Fig. 8a), which contribute to ethylene polymerization. The average number of active centers per one pore, however, decreases with increasing fraction of small pores (Fig. 8b). In the case of very small pores, some of them do not contain an Cr(II)–Cr(IV) ensemble; they are empty or contain only one type of active center, *i.e.*, only Cr(II) or only Cr(IV) (Fig. 8c). These pores and the Cr ions present in them do not contribute to the polymerization of ethylene. The pore walls make the silica surface discontinuous and form obstacles on the silica surface. Computer simulations of ethylene polymerization by the CPM give results (Fig. 7b) exhibiting the same trends as the experimental ones (Fig. 7a). The simulation was performed with 250 Cr(II) ions and 250 Cr(IV) ions randomly distributed over the silica surface with 25×10^6 adsorption sites, but randomly divided into regions by an increasing number of obstacles. In real silica, some pores are isolated but some pores are randomly connected and thus unifying their surface into one region. This was also taken into consideration by the computer simulation.



a) Active centers distribution in the very large pores



b) Active centers distribution in the medium size pores



c) Active centers distribution in very small pores

Fig. 8. Schematic presentation of the distribution of active centers in large, medium and small pores (**D** = = Cr(II) and **A** = Cr(IV)).

Polyethylene structure formation

The many details of the polymer structure can be predicted by the CPM. The purpose of this article, however, was not to present such details, which were introduced elsewhere.[23] Only some important issues will be discussed.

The most important structural characteristics of any polymer are the number (X_n) and mass (X_w) average degrees of polymerization and the molecular mass distribution presented as the ratio X_w/X_n. According to the CPM, it can be predicted that X_n is proportional to the length of the percolation path L_a between Cr(II) and Cr(IV) sites (Fig. 3 and Eq. (7)). The value of L_a is proportional to the surface area of the support (S) and inversely proportional to the square root of surface concentration of chromium active centers, *i.e.*, Cr(II) and Cr(IV), which depends on the chromium loading (Cr_0) and the fraction (f) of the activated chromium atoms (Eq. (4)). The computer simulations based on the CPM show that the degree of polymerization (X_n) has a lower value in the case of high initial concentrations of active centers (Fig. 9).

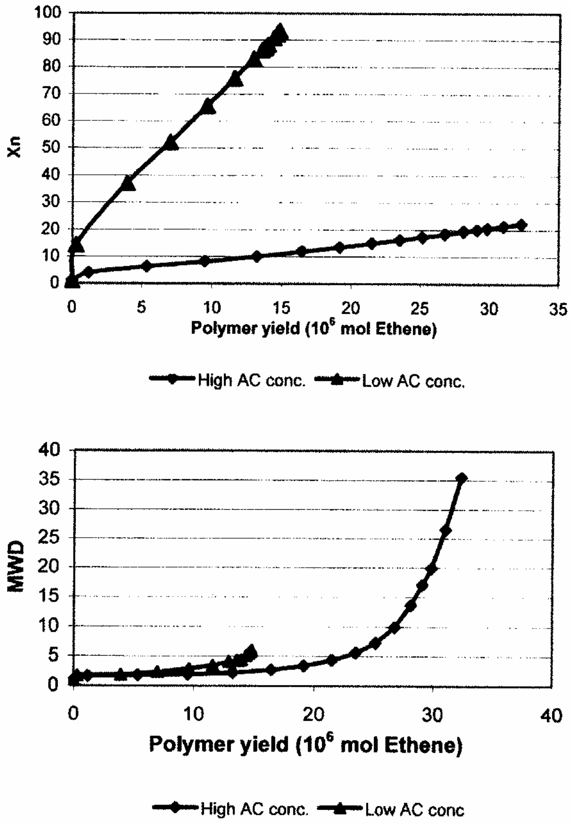


Fig. 9. Computer simulation of the effect of polymer yield on X_n and MWD for high and low concentrations of active centers (AC, *i.e.*, Cr(II) and Cr(IV)).

Furthermore, according to the CPM, it can be predicted that chromium AC are consumed during the polymerization. Hence, the initial distance between the AC centers at the beginning of polymerization is low. Since the concentration of AC decreases during the polymerization, the distances between the remaining ones increase with time. Consequently, according to the CPM, X_n should increase during the polymerization. These predictions have been confirmed experimenttally (Fig. 2, left) and by computer simulation (Figs. 2 and 9).

The computer simulations based on the CPM show that the X_w/X_n ratio, *i.e.*, the MWD, increases with the initial concentration of AC and polymer yield (Fig. 9).

It is known that the concentration of AC increases with increasing Cr loading, the concentration of hydroxyl groups on the silica, the activation temperature, the polymerization temperature, the presence of titanium in silica, *etc*. In all these cases, the CPM predictions that X_n should decrease and the MWD should be broader have been confirmed experimentally.[4]

According to the CPM, it can be predicted that the polymer chains are terminated by an unsaturated bond and a methyl group (Scheme 1). Furthermore, it can be expected that the initially formed *α*-olefin oligomers can be co-adsorbed and copolymerized with ethylene, producing short and the long chain branches. These predictions have been confirmed experimentally.[24]

CONCLUSIONS

The CPM is in good agreement with the experimental data on the ethylene polymerization by supported CrO_x systems. It gives reasonable answers to all the open questions mentioned in the introduction. In the previous work of this series,[2] the answers to the questions (1) thorough (4) were given. In this work, the answers to the remaining questions, *i.e.*, (5) thorough (7), are presented. Thus, concerning question (5), there is no induction period, or it is very short, if both active centers, *i.e.*, Cr(II) and Cr(IV), are present at the initial stages of polymerization. Otherwise, some induction period is necessary for ethylene adsorption and formation of active centers, *i.e.*, reduction of Cr(VI) to Cr(IV) and to Cr(II). The concerning question (6), the broad MWD distribution of polyethylene is due to the fact that initially the charge percolation occurs between Cr(II) and Cr(IV) sites close to each other on the silica but later, more separated Cr(II) and Cr(IV) sites are included. Hence, short oligomers are formed during the initial stage, but the very long polyethylene chains are formed during the final stages of polymerization. The role of the support (question (7)) is to deform the ethylene molecules, to concentrate them, to orient them correctly and to enable their contact with Cr, thus facilitating the polymerization. Furthermore, the distribution of active chromium species on the silica surface, as well as silica surface discontinuities, has a great influence on the polymerization activity and the polyethylene structure. The predictions by the calculation and Monte-Carlo simulation based on the CPM are in the agreement with the empirical findings.

ИЗВОД

МЕХАНИЗАМ ПОЛИМЕРИЗАЦИЈЕ ПЕРКОЛАЦИЈОМ НАЕЛЕКТРИСАЊА И СИМУЛАЦИЈА ЦИГЛЕР–НАТА ПОЛИМЕРИЗАЦИЈЕ. ДЕО VII. УТИЦАЈ РАСПОДЕЛЕ АКТИВНИХ ЦЕНТАРА ХРОМА НА СИЛИЦИЈУМ ДИОКСИДУ НА ПОЛИМЕРИЗАЦИЈУ ЕТИЛЕНА

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Механизам перколације наелектрисања (CPM) за полимеризацију олефина у присуству једињења прелазних метала је примењен за тумачење полимеризације етилена помоћу оксида хрома који је нанет на силицијум диоксид. У претходном раду ове серије приказане су основне поставке и механизам полимеризације. У овом раду је потврђена сагласност CPM са емпиријским налазима. Механизам перколације наелектрисања је примењен за објашњење: појаве индукционог периода; деактивације активних центара и образовање олигомера; утицаја концентрације хрома на силицијум диоксиду, дисконтинуитета површине и величине пора силицијум диоксида на полимеризацију и настајање структуре полимера. Изведен је математички модел који објашњава утицаје односа CrO_x/SiO_2 на продуктивност Филипсових катализатора за полимеризацију етилена. Емпиријски резултати су, такође, потврђени компјутерским симулацијама.

(Примљено 22. септембра 2006, ревидирано 13. јуна 2007)

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